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XVII.

RESEARCHES ON THE COMPLEX INORGANIC ACIDS.

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(Continued from Vol. XVII. p. 90.)

Presented May 9th, 1883.

The compounds which I have hitherto described may be embraced under the general formula

$$m\,R\,O_3 \,.\, 2\,R'_2O_5 \,.\, p\;R''_2O.$$

in which m may represent any even number from 10 to 48 inclusive, p the number of molecules of base (old style), R an atom of tungsten or molybdenum, and R′ one of phosphorus or arsenic. I shall now proceed to show that these results may be generalized in a variety of different ways, and, further, that there are other typical formulas, perhaps less general than that above given, but still embracing many interesting and instructive special cases.

HYPOPHOSPHO-MOLYBDATES.

Hypophospho-molybdate of Ammonium. — When solutions of 14 : 6 acid ammonic molybdate and sodic hypophosphite are mixed, no precipitate is formed, but the liquid takes a fine blue color from the partial reduction of molybdic teroxide to Mo_2O_5. On addition of chlorhydric acid and stirring for a short time, a large quantity of a crystalline salt separates. This is to be filtered off, well drained by the filter-pump, and washed with cold water, in which it is not very soluble. When perfectly pure and free from Mo_2O_5 the salt presents colorless prismatic crystals, which are readily soluble in hot water. The solution, at first pale blue, speedily assumes a deeper tint; with cold water a colorless strongly acid solution may be obtained, and with such the reactions here given were obtained. Baric chloride gives no precipitate alone, but after adding ammonia a colorless salt is thrown down, which is at first flocky, but which soon becomes fine-grained granular-crystalline. Strontic and calcic chlorides behave in a similar manner, but the calcic precipitate does not form so rapidly. Manganous sulphate gives no precipitate alone, but after adding ammonia a white flocky salt is formed, which becomes yellowish on standing. Cupric sulphate behaves in the same manner; the precipitate after the addition of ammonia is green and flocky. The mixture with solution of copper is not reduced on boiling, either alone or after addition of chlorhydric acid. The solution of the hypophospho-molybdate gives a canary-yellow precipitate with mercurous nitrate, and a nearly white precipitate with argentic nitrate, which soon becomes gray and finally black. Thallous nitrate gives a white flocky precipitate. When the dry salt is heated, it becomes at first black and fumes slightly, but on further heating it melts to a dark blue mass which gives off a little molybdic teroxide on heating to redness. The fused mass dissolves readily in hot water, forming a deep blue solution which has an acid reaction, and gives with magnesia-mixture the characteristic ammonio-magnesic phosphate. The effect of heat is represented by the equation

$$8\,MoO_3 \,.\, 2\,\{H_2 \,.\, PO \,.\, OH\}\; 2 \,.\, (NH_4)_2\,O + 2\,H_2O = \\ 8\,MoO_3 + P_2O_5 + 3\,H_2 + 2\,(NH_4)_2\,O + H_2O.$$

In the analyses the loss by ignition corresponds to $2\,(NH_4)_2O + H_2O + 3\,H_2$, and the residual mass to $8\,MoO_3 + P_2O_5$, when the ignition is made with sodic tungstate. In this salt, —

1.3172 gr. lost on ignition with WO_4Na_2 0.1329 gr. = 10.09 % H_2O, $(NH_4)_2O$, and H.
1.0764 gr. lost on ignition with WO_4Na_2 0.1086 gr. = 10.09 % H_2O, $(NH_4)O$, and H.
1.2369 gr. gave 0.1836 gr. NH_4Cl = 7.21 % $(NH_4)_2O$.
1.2850 gr. " 0.0918 gr. $(NH_4)_2O$ by titrition = 7.15 % "
2.4322 gr. " 0.3860 gr. $P_2O_7Mg_2$ = 9.42 % PO_2H_3.
1.6217 gr. " 0.2578 gr. " = 9.30 % PO_2H_3.

The analyses lead to the formula

$$8\,MoO_3 \,.\, 2\,\{H_2 \,.\, PO \,.\, OH\}\; 2\,(NH_4)_2\,O + 2\,aq,$$

which requires: —

		Calc'd.	Mean.	Found.	
$8\,MoO_3$	1152	80.89	80.97	—	—
$2\,PO_2H_3$	132	9.27	9.36	9.42	9.30
$2(NH_4)_2O$	104	7.31	7.18	7.21	7.15
$2\,H_2O$	36	2.53	2.49	2.47	2.52
	1424	100.00	100.00		

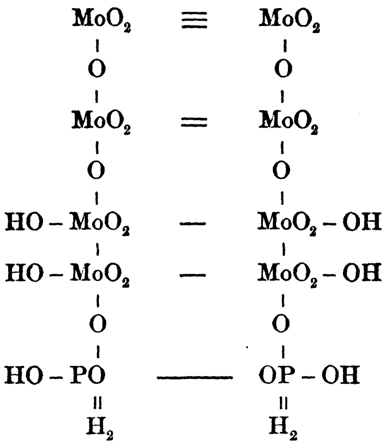
In computing the results of the analyses the loss of weight by ignition, 10.09 %, is of course taken to represent $2\,(NH_4)_2O + H_2O + 3\,H_2$, in accordance with the equation given above. In the analyses the quantity of hypophosphorous acid was determined by dissolving the salt in a solution of sodic carbonate, and then adding bromine, which with the aid of heat readily converts the hypophosphorous into phosphoric acid. The quantity of the former could not be determined by means of potassic hypermanganate in an acid solution. Bromine does not act sensibly upon acid solutions, and even an excess of nitric acid effects an imperfect oxidation. These facts, taken in connection with the relations of the salt to solutions of copper and silver, seem to show that the stability of hypophosphorous acid is increased by its combination with molybdic teroxide. The salt has, as stated, a strong acid reaction, and the limit of the basicity of this class of compounds still remains to be determined. The formula may also be written: —

$$8\,MoO_3 \,.\, 2\,\{H_2 \,.\, PO \,.\, (NH_4O)_2\}\; 2\,H_2O + 2\,aq.$$

The constitution of hypophosphorous acid was first established by Würtz. More recent investigations in organic chemistry have shown that it is to be regarded as dihydryl-phosphinic acid, and that it forms the initial term and type of an extensive series of organic acids, in which the two atoms of hydrogen attached to the phosphorus are replaced by methyl, phenyl, &c., and in which also arsenic may replace phosphorus. I do not propose at present to proceed further in this particular line of research, but will content myself with the statement that a solution of dimethyl-arsinic (kakodylic) acid gives immediately in one of 14 : 6 acid ammonic molybdate a beautiful colorless crystalline precipitate. It can hardly be doubted that this is a dimethyl-arsino-molybdate belonging to the general type represented by the formula

$$m\,MoO_3 \,.\, 2\,\{(CH_3)_2 \,.\, AsO \,.\, (OH)\}\; n\,(NH_4)_2O.$$

The structural formula of the hypophospho-molybdate above described, or rather of the corresponding acid, may be written, in accordance with the general principles already assumed, as follows: —



$$\begin{array}{ccc}
\mathrm{MoO_2} & \equiv & \mathrm{MoO_2} \\
| & & | \\
\mathrm{O} & & \mathrm{O} \\
| & & | \\
\mathrm{MoO_2} & = & \mathrm{MoO_2} \\
| & & | \\
\mathrm{O} & & \mathrm{O} \\
| & & | \\
\mathrm{HO-MoO_2} & - & \mathrm{MoO_2-OH} \\
| & & | \\
\mathrm{HO-MoO_2} & - & \mathrm{MoO_2-OH} \\
| & & | \\
\mathrm{O} & & \mathrm{O} \\
| & & | \\
\mathrm{HO-PO} & \text{———} & \mathrm{OP-OH} \\
\| & & \| \\
\mathrm{H_2} & & \mathrm{H_2}
\end{array}$$

In this formula the acid is supposed to correspond to the ammonium salt described.

HYPOPHOSPHO-TUNGSTATES.

The salts of this series are not very well defined as regards their physical properties, and it is difficult to obtain any single one in a state of perfect purity. They are most readily prepared by boiling acid tungstates with a solution of hypophosphorous acid, and appear to be in general very soluble in water, yielding sometimes thick syrupy liquids, and sometimes gelatinous masses more or less colored by the partial reduction of tungstic teroxide.

Potassic Salt. — When a strong solution of hypophosphorous acid is mixed with one of 12 : 5 acid sodic tungstate, the liquid becomes turbid and yellowish, and after a short time gelatinizes to a pale yellow mass. This is to be dissolved in boiling water, and a solution of potassic bromide added, which after a short time gives a white crystalline precipitate, to be drained upon the filter-pump, redissolved in hot water, again crystallized, drained, washed with cold water, and dried on woollen paper. As thus prepared, the salt presented small colorless granular crystals, soluble in hot water to a somewhat turbid strongly acid liquid, which effervesced with alkaline carbonates. The solution gave no precipitate with cupric sulphate, and no copper was reduced on boiling either with or without chlorhydric acid. Argentic nitrate gave a turbid white solution; on boiling, silver was reduced. Mercurous nitrate gave a white flocky precipitate, which on boiling became yellow, and finally dirty greenish yellow, without reduction of mercury. Baric chloride gave a white precipitate of indistinct feathery crystals. When heated in a porcelain crucible the salt became blue, and finally white, giving off a sharp acid smell. The residue dissolved in water, in part at least, forming a strongly acid solution. Of this salt

$$\left\{\begin{array}{l}1.2295 \text{ gr. lost on ignition } 0.0340 \text{ gr.} = 2.76\ \% \text{ water and hydrogen.}\\ 1.2295 \text{ gr. gave } 1.1172 \text{ gr. } WO_3 + P_2O_5 = 90.84\%\end{array}\right.$$
0.7272 gr. lost on ignition with WO_4Na_2 0.0203 gr. = 2.79%
1.5110 gr. gave 0.1921 gr. $P_2O_7Mg_2$ = 7.57% PO_2H_3

The analyses lead to the formula

$$18\ WO_3 \,.\, 6\ \{H_2 \,.\, PO \,.\, OH\}\ 4\ K_2O + 7\ aq,$$

which requires: —

		Calc'd.		Found.	
18 WO_3	4176	82.31	90.11	82.71	90.28
6 PO_2H_3	396	7.80		7.57	
4 K_2O	376	7.41		7.42	
7 H_2O	126	2.48		2.45	
	5074	100.00		100.15	

In the analysis the hypophosphorous acid was determined by oxidation with bromine in an alkaline solution and precipitation with magnesia-mixture. The formula given may be written, with equal probability,

$$18\ WO_3 \,.\, 6\ \{H_2 \,.\, PO \,.\, OK\}\ K_2O \,.\, 3\ H_2O + 7\ aq,$$

since the assignment of the fixed base is purely arbitrary; other arrangements are also possible. I am disposed to regard the salt as acid, with the formula

$$2\ (6\ WO_3 \,.\, 2\ \{H_2 \,.\, PO \,.\, OH\}\ 2\ K_2O) + \\ 6\ WO_3 \,.\, 2\ \{H_2 \,.\, PO \,.\, OH\}\ 2\ H_2O + 5\ aq,$$

so that the type of the corresponding acid, setting aside the question of basicity, will be

$$6\ WO_3 \,.\, 2\ \{H_2 \,.\, PO \,.\, OH\}\ 2\ H_2O.$$

The structural formula of such an acid will be similar to that already given in the case of the hypophospho-molybdate described. Further investigation may, however, show that the more complex formula must be admitted. I content myself with proving that there is at least one class of hypophospho-tungstates. In computing the direct results of the analyses I have assumed that, as in the case of the corresponding molybdenum compounds, the complex $2\ \{H_2 . PO . OH\}$ is oxidized to P_2O_5 wholly at the expense of two molecules of WO_3 reduced to W_2O_5, which last is then again oxidized to $2\ WO_3$ by heating in air. This assumption appears to be justified by the changes of color observed on heating the salt. The actual loss of weight observed then corresponds to water and hydrogen only, the percentage of hydrogen being calculated from that of $P_2O_4H_6$.

When tungstic hydrate in excess is boiled with a solution of sodic hypophosphite, it dissolves very readily, giving a pale blue solution which yields on evaporation a thick syrupy liquid. This solution gives precipitates with $BaCl_2$, NH_4Cl, and KBr, and will furnish a convenient starting-point for further investigation. It does not oxidize readily in the air, even after long standing. A solution of dimethyl-arsinic acid gives with one of 12 : 5 acid sodic tungstate a beautiful colorless crystalline precipitate. I have not studied this compound, from want of proper facilities for work of the kind. It will, I think, prove to be a dimethyl-arsino-tungstate, coming under the general formula

$$m\ WO_3 . 2\ \{(CH_3)_2 . AsO . OH\}\ n\ Na_2O,$$

and we may reasonably expect an extensive series of analogous compounds, in which other radicals take the place of methyl.

PHOSPHOROSO-MOLYBDATES.

Since phosphorous acid is now to be regarded as hydryl-phosphinic acid with the formula

$$\{H . PO . (OH)_2\},$$

the existence of a class of phosphoroso-molybdates and of phosphoroso-tungstates appeared, to say the least, a probable inference from that of the hypophospho-compounds already described.

Phosphoroso-molybdate of Ammonium. — When a solution of phosphorous acid — as prepared by the reaction of phosphorous chloride with water — is added to one of 14 : 6 acid ammonic molybdate, a very pale yellow indistinctly crystalline precipitate is formed, which is insoluble in cold water. Hot water dissolves it only in a small proportion, but gives a milky emulsion, which settles very slowly. For analysis the salt was drained on a filter-pump, well washed with cold water, and finally dried on woollen paper. Of this salt, —

1.9695 gr. gave 0.0980 gr. $(NH_4)_2O$ = 4.97% by titrition.
1.1425 gr. " 0.0559 gr. " = 4.89% "
0.9301 gr. lost on ignition with WO_4Na_2 0.1225 gr. = 13.17%
1.2722 gr. gave 0.1374 gr. $P_2O_7Mg_2$ = 7.97% PO_3H_3

The analyses correspond fairly well with the formula

$$24\ MoO_3 . 4\ \{H . PO . (OH)_2\}\ 4\ (NH_4)_2O + 17\ aq,$$

which requires: —

	Calc'd.		Found.	
24 MoO_3	80.41	88.04	79.88	87.85
4 PO_3H_3	7.63		7.97	
4 $(MH_4)_2O$	4.84		4.89	4.97
17 H_2O	7.12		7.22	
	100.00			

The salt certainly contained a little phospho-molybdate, to which the faint yellow tint was probably due. It is very difficult to obtain a solution of phosphorous which is absolutely free from phosphoric acid. With respect to the formula I remark that the number of molecules of water may be purely accidental, and that there is at present no sufficient reason for rejecting the simpler expression

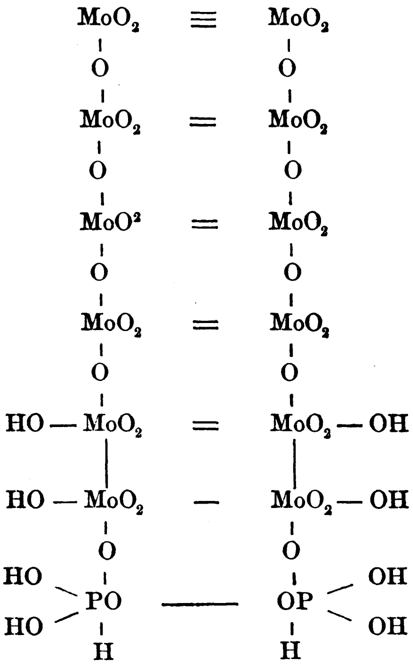
$$12\ MoO_3 . 2\ \{H . PO . (OH)_2\}\ 2\ (NH_4)_2O + x\ aq.$$

The type of the acid is then

$$12\ MoO_3 . 2\ \{H . PO . (OH)_2\}\ 2\ H_2O.$$

A solution of baric chloride boiled with the phosphoroso-molybdate decomposes it more or less completely, giving a white very fine-grained crystalline salt. Under the same circumstances argentic nitrate gives a nearly colorless flocky substance, which quickly becomes darker, and finally assumes a dull violet color. Mercurous nitrate yields a clear pale yellow flocky salt; the phosphoroso-molybdate does not reduce a solution of mercuric chloride even on boiling. Cupric sulphate dissolves the salt to a clear blue liquid. Manganous sulphate also dissolves it, forming a colorless solution. Alkaline hydrates dissolve it very readily to colorless liquids. The salt is readily decomposed by heating in a porcelain crucible, and fuses at a low red heat, giving off vapors of molybdic teroxide. The fused mass on cooling is bluish gray. It dissolves readily in water to a deep blue liquid, which has a strongly acid reaction, and gives with magnesia-mixture the reaction for phosphoric acid.

The structural formula of the acid corresponding to the ammonium salt may be written provisionally: —



If we accept the views now generally received as to the constitution of hypophosphorous and phosphorous acids, the hypophospho-molybdates, hypophospho-tungstates, and phosphoroso-molybdates furnish a much needed demonstration of the fact, that in this whole class of compounds part at least of the hydroxyl is united to phosphorus directly, and a part only to tungsten or molybdenum. This will appear at once from the formulas for the two acids, since these cannot be broken up into simpler expressions,

$$\{H_2 . PO . OH\}, \quad \text{and} \quad \{H . PO . (OH)_2\},$$

or from the structural formulas which I have given. I shall return to this point hereafter, and give additional proofs of the twofold mode of combination of hydroxyl.

Further investigation will almost certainly show that the homologues of hydryl-phosphinic or phosphorous acid will also form complex acids with tungstic and molybdic teroxides. Thus methyl-phosphinic acid $\{CH_3 . PO . (OH)_2\}$ should form at least one series of each of the general types: —

$$m\, MoO_3 . \{CH_3 . PO . (OH)_2\}\; n\, H_2O.$$
$$n\, WO_3 . \{CH_3 . PO . (OH)_2\}\; p\, H_2O.$$

In these cases arsenic, and perhaps antimony, may replace phosphorus. Phosphoroso-tungstates may be formed by the action of phosphorous acid upon acid tungstates. The only salt obtained at present appears to have the formula

$$12\, WO_3 . 2\, \{H . PO . (OH)_2\}\; 2\, K_2O + 12\, aq.$$

I propose to return to this special point when describing the related groups of arsenoso-tungstates and antimonoso-tungstates and the corresponding molybdates. In the analysis of the phosphoroso-molybdate of ammonium the phosphorous acid was determined by dissolving the salt in an excess of a solution of sodic carbonate, oxidizing with bromine, and precipitating with magnesia-mixture.

VANADIO-MOLYBDATES.

The general analogy between vanadic, arsenic, and phosphoric pentoxides suggested to me the possibility of forming series of vanadio-molybdates and vanadio-tungstates, belonging to types of a character similar to those of the phospho-molybdates and phospho-tungstates already described. I shall now show that such compounds may readily be formed by processes identical in principle with those which yield compounds of phosphoric and arsenic oxides with molybdic teroxide.

Vanadio-molybdates are formed when vanadic pentoxide V_2O_5 is digested with solutions of alkaline molybdates, more especially with the acid salts of potassium, sodium, or ammonium. The solution quickly becomes yellow, then, on heating, orange, and finally passes in many cases to deep orange-red. The vanadic oxide or acid employed must be perfectly free from vanadic dioxide, as this is also readily dissolved. The resulting compound then belongs to the class of triple complex acids, and contains both oxides of vanadium united to molybdic oxide. I shall return to these compounds in due time, and meanwhile shall refer to them under the name of vanadico-vanadio-molybdates. The presence even of a small quantity of vanadic dioxide may usually be detected by a peculiar greenish shade of color, easily recognized when once seen. This tint disappears when the solution is heated for a short time with bromine water or nitric acid, which readily oxidize the lower oxides of vanadium.

Vanadio-molybdates are also formed when solutions of alkaline vanadates and molybdates are heated together, and more readily when an excess of acid is present. The mixed solution then assumes at once a deep orange-red color.

The same salts are also formed when molybdic oxide, MoO_3, is boiled with a solution of an alkaline vanadate or meta-vanadate. Ammonic meta-vanadate, VO_3NH_4, may now be had in commerce in a state of very considerable purity, and has served as the starting point for much of my work. A solution of this salt readily dissolves molybdic oxide, forming one or more vanadio-molybdates, only in this case there is a tendency to a kind of supersaturation, a large excess of molybdic oxide being dissolved and separating from the liquid on cooling.

Finally, vanadio-molybdates may be formed by the decomposition of phospho-vanadio-molybdates, a class of triple compounds also to be described.

The vanadio-molybdates of the alkaline metals are in general readily soluble in water. They are highly crystalline, have a yellow or greenish yellow, sometimes orange-yellow or orange-red color, and give in many cases crystalline precipitates with salts of the alkaline earths, of silver, and of thallium. They are not decomposed by boiling with excess of acid, and are usually very stable, except in the presence of reducing agents.

Analytical Methods. — The quantitative separation of molybdenum from vanadium presented a new problem in analytical chemistry, the solution of which cost much time and labor. It may be effected in two different ways. When the vanadium is wholly or partially in the form of vanadic dioxide, VO_2, it is to be oxidized by heating the concentrated solution with nitric acid. An alkaline carbonate is then to be added until the solution is nearly neutral, when the vanadic and molybdic oxides may be precipitated together by means of mercurous nitrate and mercuric oxide, precisely as in the estimation of tungstic oxide already described. The precipitate of mercurous vanadate and molybdate and mercuric oxide is to be filtered upon a paper filter. After drying, the filter and contents may be heated together in a platinum crucible, with free access of air. When the process is carefully conducted, the filter may be completely incinerated with great ease, and without loss of molybdic oxide from volatilization. A weighed quantity of fused and pulverized neutral sodic tungstate is then to be added, when the crucible may be heated to redness, and the mercurous and mercuric oxides completely expelled. A second heating and weighing are always advisable. In this manner the sum of the weights of molybdic and vanadic oxides is obtained. To determine the quantity of vanadic oxide alone, the same process is to be repeated; only after burning off the filter the mass is to be carefully heated with a free supply of air to act mechanically until the whole of the molybdic oxide is volatilized and vanadic oxide remains as an orange-brown liquid, and, after cooling, as a crystalline mass. The complete expulsion of the molybdic oxide requires long heating, at a full red heat. The vanadic oxide is not volatile, but it has the inconvenient habit of creeping up the sides and over the edge of the crucible, — a habit for which there appears to be no remedy. The weight of the molybdic oxide may then be determined by difference. This method gives good results, and in some cases may be used with advantage.

Another method is the following, which applies directly to the vanadio-molybdates of the alkaline metals, and to those of the alkaline earths, after the separation of the base. Ammonia is to be added in excess to the solution, which is then to be boiled for a few minutes, so as to convert the salt into a mixture of an alkaline vanadate and molybdate. A saturated solution of ammonic chloride is then added in very large excess, after which the liquid must be concentrated by continued boiling until reduced to a relatively small volume. The solution must then be allowed to stand for twenty-four hours, when a greater or less deposit of ammonic meta-vanadate will have formed in colorless crystals.* These crystals are to be brought upon an asbestos filter, and washed with a cold saturated and pure solution of ammonic chloride. The vanadic pentoxide may then be found by carefully igniting the salt with free access of air. It is, however, better to dissolve the salt upon the filter with boiling water, reduce the solution by means of a current of sulphydric acid gas after adding a little sulphuric acid, filter, and titrate with potassic hypermanganate. The clear blue solution contains vanadic dioxide only. The end reaction is tolerably sharp in dilute solutions — say 0.25 gramme — of VO_2 in 250 c. c. of water. The reason for adopting the method of titrition is, that the ignition of ammonic meta-vanadate, even when conducted with great care, usually yields a mixture of vanadic pentoxide and dioxide, which it is difficult to oxidize completely. The precipitation of ammonic meta-vanadate by ammonic chloride is, as is well known, not absolutely complete, but the results of the analyses are on the whole fairly good.

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* The best commercial chloride of ammonium always contains iron not precipitable by ammonia. If bromine water be added first to the boiling solution, ammonia in small quantity separates the iron completely.

It is sometimes more advisable to employ a combination of the two methods described. After precipitating the two oxides by means of mercurous nitrate and mercuric oxide, the greater part of the molybdic oxide may be expelled by heat, after which the mixture of oxides, which now consists chiefly of vanadic pentoxide, may be dissolved in ammonia and treated with ammonic chloride in the manner above described. The quantity of molybdic oxide is most easily estimated by difference, the sum of the weights of the two oxides being determined by the method given above. It is not possible to reduce the vanadic pentoxide in the vanadio-molybdates to vanadic dioxide by means of sulphydric acid gas, by sulphurous oxide, or by any other reagent which I have tried, without at the same time reducing a portion of the molybdic teroxide to the blue oxide Mo_2O_5. This difficulty may however be overcome by first adding phosphoric acid to the solution in quantity about equal to the weight of the salt analyzed. After the addition of a little sulphuric acid the reduction of the vanadic pentoxide may be effected either by boiling with a solution of sulphurous oxide, or by passing sulphydric acid gas for some time through the hot solution of the salt.

In separating vanadic from molybdic oxide by means of ammonic chloride it is necessary to keep the solution always slightly alkaline by the occasional addition of a little ammonia, since, as soon as the liquid becomes acid by the dissociation of the ammonium salts present, a vanadio-molybdate is again formed in greater or less quantity. To resolve a vanadio-molybdate into a mixture of vanadate and molybdate, it is necessary to employ an excess of free ammonia, and also to heat the solution. Actual boiling is most advantageous.

Another method of estimating vanadic oxide in the presence of molybdic teroxide consists in boiling the compound with strong chlorhydric acid, passing the chlorine set free into a solution of potassic iodide, and then determining the free iodine volumetrically by sodic hyposulphite and starch. I have not actually employed this method, however, though it gives excellent results in the analysis of the vanadio-tungstates.

It will be convenient to speak in this place of the best method of determining vanadium in alkaline vanadates without special reference to its separation from other elements. I find that this estimation may be effected with great accuracy by first oxidizing any lower oxide which may be present by means of nitric acid to vanadic pentoxide, and then precipitating the faintly acid solution by mercurous nitrate and an excess of mercuric oxide at a boiling heat. Precipitation by mercurous nitrate alone was long since suggested by Berzelius, but the addition of mercuric oxide to render and to keep the solution neutral makes precisely the difference between a very accurate and an only tolerably good result. The precipitate may be collected upon a paper filter, and after washing with hot water ignited with free access of air. On cooling, a fine orange-brown crystalline mass of vanadic pentoxide remains. The filtrate from the precipitated oxides contains no appreciable trace of vanadium. The great facility with which a solution of vanadic pentoxide containing free chlorhydric acid is reduced by ferrous salts, suggested the possibility of determining vanadium by titrition with ferrous sulphate, a solution of potassic ferricyanide being employed to determine the point of complete reduction.

A special study of this process was made in my laboratory by my assistant, Mr. Charles A. French, to whom the following details are exclusively due. The solution containing vanadic pentoxide is to be concentrated, and chlorhydric acid solution containing about one tenth of its weight of pure acid added in large excess. After nearly saturating with a solution of ferrous or ammonio-ferrous sulphate of known titre, the solution is to be heated nearly to boiling, and the titrition then completed with the ferrous salt, the end reaction being determined by trial drops upon a porcelain plate with a very dilute solution of potassic ferricyanide. Of this solution two drops of the ordinary laboratory reagent in a test-tube full of water give an appropriate strength. The process may be varied by adding the ferrous solution in excess, then titrating back by means of potassic dichromate of known titre, and finally adding the ferrous salt until the end reaction with ferricyanide is obtained. The ferrous solution may contain with advantage 0.005 gr. of iron in one cubic centimeter. A sample of potassic divanadate containing no other impurity than a little potassic nitrate gave, by the gravimetric process above described, 65.12% V_2O_5. In three successive titritions with ammonio-ferrous sulphate Mr. French found 65.16, 65.27, and 64.95%.

As ammonic meta-vanadate is now largely used in the manufacture of aniline black, and has become an article of commerce, the method of titrition described above may perhaps find useful application in technical laboratories, as the end reaction in titrating with hypermanganate is not very sharp. I have in my work employed it in several cases as a check upon other methods.

In the analyses of vanadio-molybdates it is best to determine the alkalies by difference, as in the cases of the phospho-molybdates and phospho-tungstates. As in these cases also ammonia and water are best determined together by ignition with a weighed portion of neutral sodic tungstate, WO_4Na_2, a method suggested by Dr. F. A. Gooch for the whole class of phospho tungstates and phospho-molybdates of ammonium; only in the case of the vanadio-molybdates and other salts containing both molybdenum and vanadium, it is necessary to be especially careful in igniting with the tungstate, because molybdic teroxide is sometimes given off before the complete fusion of the tungstate with the salt.

6 : 1 *Series.* — A solution of ammonic meta-vanadate, VO_3NH_4, readily dissolves molybdic teroxide on boiling, forming a deep orange-yellow solution. The liquid on standing deposits a very beautiful lemon-yellow salt, in sharp octahedral crystals, which are soluble in a rather large excess of cold water without sensible decomposition. The solution, on spontaneous evaporation, yields the salt without change. Of this salt, —

1.1349 gr. lost on ignition with WO_4Na_2 0.1806 gr. = 15.91%
1.3220 gr. " " " " 0.2128 gr. = 16.09%
1.5022 gr. " " " " 0.2412 gr. = 16.05%
1.2477 gr. gave 0.2201 gr. NH_4Cl = 8.57% $(NH_4)_2O$
1.3822 gr. " 0.2439 gr. " = 8.57% "
1.2847 gr. " 0.1893 gr. V_2O_5 by $KMnO_4$ = 14.73%

The analyses lead to the formula

$$6\ MoO_3 \,.\, V_2O_5 \,.\, 2\ (NH_4)_2O + 5\ aq,$$

which requires: —

		Calc'd.	Found.		
6 MoO_3	864	69.62			
V_2O_5	183	14.74	14.73		
2 $(NH_4)_2O$	104	8.39	8.57	8.57	
5 H_2O	90	7.25	7.34	7.52	7.48
	1241	100.00			

The reactions of a solution of this salt in cold water are as follows. No precipitate with salts of copper, zinc, manganese, and cadmium. Argentic nitrate gives a flocky yellow precipitate, with a tinge of buff. Mercurous nitrate gives a bright yellow precipitate. Thallous nitrate gives a very pale yellow flocky precipitate, which does not become crystalline on standing. Baric chloride gives no precipitate at first, but after a short time very beautiful sharp octahedral crystals: after longer standing small pale yellow very distinct prismatic crystals also appear in the solution. Strontic chloride gives, after some days, very well defined pale yellow prismatic crystals. The solution of the vanadio-molybdate gives a rather dull yellow flocky precipitate with hydro-chloride of brucin, and a bright yellow one with hydro-chloride of strychnin. No precipitate is formed at first with potassic bromide, but after some days beautiful very well defined granular crystals are deposited in quantity.

The solution of the salt has a strongly acid reaction. The mercurous salt is decomposed by dilute chlorhydric acid, with formation of mercurous chloride and a yellow acid solution, doubtless of the acid of this series. The acid was decomposed by spontaneous evaporation, and did not yield crystals.

It appears unnecessary to give a structural formula for the salt described, since we may regard V_2O_5 as simply replacing P_2O_5, and with the same function as this last, so that the structural formulas already given for the phospho-tungstates will apply to the present case also.

Eight Atom Series. — When acid ammonic molybdate is dissolved, and vanadic pentoxide is added in small quantities at a time, the boiling solution quickly becomes yellow, and then orange. If the vanadic oxide is not perfectly free from dioxide, VO_2, a little bromine water should be employed to complete the oxidation. If a solution of baric chloride be mixed with the rather dilute and warm solution, no precipitate is formed at first, but after a few seconds an abundance of beautiful yellow well-defined crystals appears. These crystals are very sharp octahedra, and strongly resemble those of one of the ammonium salts of the six-molecule series. After a time granular yellow crystals make their appearance also in large quantity. The habitus of these crystals is so different from that of the first named that the two can readily be separated when mixed. A very approximate separation can also be effected by pouring off the liquid the moment that the granular crystals begin to appear. The yellow octahedral crystals are soluble in hot water, containing a little chlorhydric acid, and may be recrystallized. When heated, the salt swells up very much, and turns black, looking like coke. Of this salt, —

1.0070 gr. lost on ignition with WO_4Na_2 0.1310 gr. = 13.00%
0.9716 gr. “ “ “ “ 0.1280 gr. = 13.17%
1.2449 gr. “ “ “ “ 0.1637 gr. = 13.16%
0.9682 gr. gave 0.6534 gr. $MoO_3 + V_2O_5$ = 67.48%
1.0162 gr. “ 0.3029 gr. SO_4Ba = 19.56%
1.0343 gr. “ 0.3072 gr. “ = 19.50%
1.0190 gr. “ 0.3023 gr. “ = 19.48%
1.0937 gr. “ 0.0998 gr. V_2O_5 = 9.12%
1.4395 gr. “ 0.1356 gr. “ = 9.37%

These analyses lead to the formula

$$16\ MoO_3 \,.\, 2\ V_2O_5 \,.\, 5\ BaO + 29\ aq,$$

or,

$$8\ MoO_3 \,.\, V_2O_5 \,.\, 3\ BaO + 8\ MoO_3 \,.\, V_2O_5 \,.\, 2\ BaO \,.\, H_2O + 28\ aq,$$

which requires: —

		Calc'd.	Found.		
16 MoO_3	2304	58.25		58.34	
2 V_2O_5	364	9.21		9.12	9.37
5 BaO	765	19.35	19.48		19.56
29 H_2O	522	13.19	12.96	13.00	13.16
	3955	100.00			

The salt is therefore to be regarded as the acid salt of the eight-atom series, and belongs to a type of which several examples have been given among the phospho-tungstates and phospho-molybdates. It may also be considered as an acid sixteen-atom salt, upon the view which I have suggested in another place as at least possibly correct. The 16 : 2 barium salt is also formed when baric chloride is added to a solution of the 6 : 1 vanadio-molybdate of ammonium already described. The last-named salt is therefore formed when vanadic pentoxide is dissolved in acid ammonic molybdate, as well as when molybdic oxide is dissolved in ammonic meta-vanadate. In the double decomposition with baric chloride at least three molecules of the 6 : 1 ammonium salt must take part. The barium salt is nearly insoluble in cold water, but is soluble in much hot water, with partial decomposition and deposition of baric molybdate. The solution in cold water reddens litmus strongly: it gives with argentic nitrate a pale, and with mercurous nitrate a bright yellow flocky precipitate.

The first determination of vanadic pentoxide in this salt was made by heat alone, the mixture of molybdic and vanadic oxides being ignited until a constant weight was obtained. In the second analysis the determination was made by titrition with ferrous sulphate after adding chlorhydric acid to the solution.

Eighteen Atom Series. — A boiling solution of ammonic metavanadate readily dissolves molybdic teroxide, MoO_3, forming a deep yellow or orange-yellow solution. When the oxide is added as long as it is readily dissolved, an olive-green liquid is obtained, from which after twenty-four hours hard tabular crystals of a pale greenish color are deposited. These crystals are decomposed by boiling water, beautiful yellow needles very slightly soluble in water, being formed, together with a greenish yellow solution which soon becomes turbid. The salt could not be purified by recrystallization, and was therefore washed with a little cold water and dried on woollen paper. Of this salt, —

0.8067 gr. ignited with WO_4Na_2 lost 0.1586 gr. = 19.66%
0.8538 gr. gave 0.2140 gr. NH_4Cl = 12.18% $(NH_4)_2O$
1.0243 gr. " 0.2526 gr. " = 11.99% "
0.7945 gr. " 0.0407 gr. V_2O_5 = 5.12%

These analyses correspond to the formula

$$18\ MoO_3 \cdot V_2O_5 \cdot 8\ (NH_4)_2O + 15\ aq.$$

		Calc'd.	Found.	
18 MoO_3	2592	74.89	75.22	
V_2O_5	183	5.29	5.12	
8 $(NH_4)_2O$	416	12.02	11.99	12.18
15 H_2O	270	7.80	7.58	
	3461	100.00		

A more extended investigation will, undoubtedly, show that the vanadio-molybdates are, to say the least, numerous. The salts which I have described are sufficient to establish a parallelism between them and the phospho-molybdates, which is the more interesting because the chemical relations of vanadium are nearer to antimony than to phosphorus and arsenic. I shall return to this point, however, in describing and discussing the class of antimonio-tungstates and antimonio-molybdates.

VANADIO-TUNGSTATES.

Vanadio-tungstates are very readily formed under conditions precisely the same as those which determine the formation of vanadio-molybdates, and which it is unnecessary to recapitulate. As a class, they have a yellow, orange, or orange-red color. They are, so far as examined, readily soluble in water, are crystalline and extremely stable in composition, in the sense at least that it is often difficult to separate the combined vanadic and tungstic oxides, though in many cases complex salts easily break up into compounds of simpler type.

Analytical Methods. — When alkaline vanadates and tungstates are simply mixed together under conditions which do not result in the formation of vanadio-tungstates, it is possible to effect the separation of the vanadic and tungstic oxides by means of a solution of ammonic chloride, which, as is well known, precipitates ammonic meta-vanadate in colorless crystals nearly insoluble in a saturated solution of ammonic chloride. This method cannot be applied directly to the separation of the two oxides when combined, as in the vanadio-tungstates, but the difficulty can be overcome by either of the following methods. An excess of ammonia is to be added to the solution, which is then to be digested, or, if necessary, boiled until the liquid becomes colorless. By this process, which, however, does not always perfectly succeed, the vanadio-tungstate is resolved into a mixture of ammonic tungstate and meta-vanadate. In place of ammonia, sodic or potassic hydrate in excess may be employed, and frequently with advantage. After the resolution of the vanadio-tungstate, as indicated by the color of the liquid, ammonic meta-vanadate may be precipitated by boiling with an excess of ammonic chloride. From the cold solution completely saturated with ammonic chloride the meta-vanadate my be separated by filtration, and the vanadic pentoxide estimated in the manner already pointed out. A variation of this process, which may often be employed with advantage, consists in fusing the vanadio-tungstate with an excess of potassic or sodic carbonate in a platinum crucible. The fused mass must be boiled with a strong solution of ammonic chloride, a drop or two of ammonia being added from time to time to keep the solution distinctly alkaline. The ammonic meta-vanadate is to be separated and treated as above. In applying these methods it is important in each case to be sure that the vanadium is exclusively in the form of pentoxide. It is therefore always advisable to add a little bromine water to the solution of the vanadio-tungstate before adding the excess of ammonia. In fusing with alkaline carbonates a little potassic or sodic nitrate may be added to the mixture in the crucible. In this manner we may avoid the error which would result from the presence of vanadic dioxide in the small quantity which often exists in consequence of the reducing agency of dust or traces of organic matter.

After a great number of trials, the methods given above are the only ones by which I have found it possible to effect even an approximate separation of vanadic and tungstic oxides in combination.

In place of the actual separation of the oxides, it is much more convenient, and I believe also in general much more accurate, to employ the following process, which permits us to estimate vanadium quantitatively in presence of tungstic, as well as of various other oxides. This process depends upon the fact that vanadic pentoxide, either free or in combination, when boiled with strong chlorhydric acid, evolves chlorine, which may be collected in a solution of potassic iodide. The iodine set free may then be estimated with great accuracy by means of sodic hyposulphite after adding a solution of starch.

The fact that vanadic pentoxide evolves chlorine on heating with chlorhydric acid was, so far as I have been able to find, first remarked by Mohr, who in his well-known work on volumetric analysis suggested as possible the method of determining vanadium which I have employed, without, however, testing it in any single case.

It is possible, in some cases at least, to determine vanadic pentoxide in the presence of tungstic oxide by titrition with hypermanganate. To the solution of the substance containing both metals, phosphoric and sulphuric acids are to be added, and the vanadic pentoxide is then to be reduced to dioxide by means of sulphydric acid gas passed into the boiling solution until complete reduction is obtained. No appreciable quantity of tungstic oxide is reduced under these circumstances. The titrition with hypermanganate may then usually, though not always, be executed, and gives a fairly good result.

Finally, the method of titrition by ferrous salts may often be used with success. The details have already been given, and do not need to be repeated.

5 : 1 *Vanadio-tungstate of Ammonium.* — When 12 : 5 ammonic tungstate is boiled with a solution of ammonic meta-vanadate an orange solution is obtained, which on evaporation deposits orange-yellow crusts of indistinct crystals. The color of this salt is somewhat dull; it is not very soluble in cold, but soluble in boiling water, and may be recrystallized without sensible decomposition. The salt becomes greenish upon the surface when dried upon woollen paper, from a slight superficial reduction of the vanadic pentoxide. Of this salt, —

1.0558 gr. gave 0.1222 gr. $(NH_4)_2O$ by titrition = 11.57%
1.1873 gr. lost on ignition 0.2922 gr. = 24.61% H_2O and NH_3
1.0558 gr. gave by titrition with $KMnO_4$ 11.09% V_2O_5

The analyses lead to the formula

$$5\ WO_3 \cdot V_2O_5 \cdot 4\ (NH_4)_2O + 13\ aq,$$

or

$$5\ WO_3 \cdot V_2O_5 \cdot 4\ (NH_4)_2O \cdot 2\ H_2O + 11\ aq,$$

if we regard the acid provisionally as 6-basic, which requires: —

		Calc'd.	Found.
5 WO_3	1160	64.99	—
V_2O_5	183	10.26	11.09
4 $(NH_4)_2O$	208	11.65	11.57
13 H_2O	234	13.10	13.04
	1785	100.00	

The percentage of vanadic oxide found is too high, but there can be no reasonable doubt as to the formula. I obtained the salt but once, and then in small quantity. The solution gives a dull yellow flocky precipitate with argentic and mercurous nitrates, and after a time a yellow crystalline precipitate with excess of potassic bromide. The ammonium salt is interesting as being probably the first term in a series. It corresponds to the phospho-molybdate

$$5\ MoO_3 \cdot P_2O_5 \cdot 3\ (NH_4)_2O \cdot 3\ H_2O + 4\ Aq.$$

The following may serve as starting points for further investigation. When normal baric tungstate, WO_4Ba, is boiled for a long time with a solution of ammonic meta-vanadate, it is very slowly dissolved to an orange-yellow solution, which on cooling gives very beautiful square tabular deep red crystals mixed with excess of baric tungstate. 12 : 5 baric tungstate dissolves more readily in the meta-vanadate, and gives a bright orange-yellow solution, which on evaporation yields fine prismatic crystals. From the above it appears probable that the tungstates of the heavy metals, both neutral and acid, will yield vanadio-tungstates by boiling with alkaline vanadates, and possibly in this manner various new series of salts may be formed. The costliness of the material for this work has prevented a more thorough study on my own part.

10 : 1 *Vanadio-tungstic Acid.* — A solution of ammonic meta-vanadate dissolves tungstic oxide readily on boiling, giving a deep orange-

yellow solution. After long boiling with an excess of the oxide, the clear deep orange filtrate gives, with a solution of chloride of trimethylammonium, on standing some hours, two distinct kinds of crystals, which are respectively yellow and deep orange-red. There are therefore, apparently at least, two different salts formed in the solution of the tungstic oxide. The solution of the ammonium salt gave with baric chloride, after some hours, sharp octahedral crystals of a yellow salt but slightly soluble even in hot water. In a second experiment, baric chloride gave at once a yellow fine-grained crystalline insoluble precipitate; but the precipitation was not complete. On boiling the mixture of oxides obtained by igniting ammonic meta-vanadate in air with 12 : 5 sodic tungstate, I obtained a greenish-orange solution. This was oxidized by boiling with nitric acid, when it became orange. On standing, the acid solution deposited a relatively large quantity of a sulphur-yellow crystalline body, which was but very slightly soluble in cold water, and required a large quantity of hot water for complete solution. This substance was drained upon the filter-pump, washed with cold water, and dried upon woollen paper. Of this preparation, —

$$\left\{\begin{array}{l} 0.8331 \text{ gr. lost on ignition } 0.1188 \text{ gr.} = 13.42\% \\ 0.8331 \text{ gr. gave } 0.7192 \text{ gr. } WO_3 + V_2O_5 = 86.03\% \end{array}\right.$$

0.9786 gr. " 0.8411 gr. " $= 85.95\%$
1.0846 gr. " 0.0718 gr. V_2O_5 $= 6.62\%$

The analyses correspond with the formula

$$10\ WO_3 \,.\, V_2O_5 \,.\, 6\ H_2O + 16\ aq,$$

which requires: —

		Calc'd.		Found.	
10 WO_3	2320	80.53	86.88	80.30	86.92
V_2O_5	183	6.35		6.62	
22 H_2O	378	13.12		13.08	
	2899	100.00			

I did not succeed in obtaining salts corresponding to the 10 : 1 acid above described by saturating the acid with alkaline bases, as mixtures of the acid with alkaline vanadates and tungstates were formed until the point of complete saturation was reached.

18 : 1 *Vanadio-tungstic Acid.* — The orange-yellow mother liquor from which the 12 : 1 acid separated gave on evaporation beautiful crystalline needles of a second acid, the formula of which is

$$18\ WO_3 \,.\, V_2O_5 \,.\, 6\ H_2O + 30\ aq.$$

Of this acid, —

$$\left\{\begin{array}{l}1.0343 \text{ gr. lost on ignition } 0.1342 \text{ gr.} = 12.97\% \text{ water.}\\ 1.0343 \text{ gr. gave } 0.0363 \text{ gr. } V_2O_5 = 3.51\%\end{array}\right.$$

$$1.2540 \text{ gr. lost on ignition } 0.1617 \text{ gr.} = 12.90\%$$

The formula requires: —

		Calc'd.		Found.		
18 WO_3	4176	83.40	87.05		83.55	87.06
V_2O_5	183	3.65			3.51	
36 H_2O	648	12.95		12.90	12.97	
	5007					

The sum of the two oxides is determined by difference, which is the most accurate method whenever applicable. In this, as in all the other vanadio-tungstic compounds analyzed, the vanadic pentoxide was determined by boiling with chlorhydric acid in the manner already described. The crystals of the 18:1 acid are readily soluble in water, and may be recrystallized without decomposition.

The compounds which I have described appear to establish a complete analogy between the vanadio-tungstates and phospho-tungstates already described. Rammelsberg[*] has described a salt which crystallizes in beautiful brown-black cubo-octahedrons, and which he obtained by saturating a commercial sodic vanadate with acetic acid and evaporating spontaneously. According to his analyses, the salt has the formula

$$(NH_4)_2O \,.\, WO_3 \,.\, 3\, V_2O_5 + 6 \text{ aq.}$$

I suspect that it contains VO_2 as well as V_2O_5. I did not succeed in preparing it by synthesis, employing pure VO_3NH_4 and $WO_4(NH_4)_2$. It may prove to be the type of an entirely new class of complex acids, and well deserves further investigation.

PHOSPHO-VANADIO-MOLYBDATES.

Triple acids of this class are formed when solutions of phospho-vanadates are digested with molybdic teroxide; when vanadio-molybdates and alkaline phosphates are heated together in solution, especially in the presence of an acid; and when vanadic pentoxide is heated with a solution of an alkaline phospho-molybdate.

The salts of this class are as a whole less stable than the vanadio-molybdates. They are, however, very well defined, and usually highly crystalline. In color they vary from an orange to a deep garnet, or ruby red. In general character they closely resemble the salts of the double compounds already described, and are often very beautiful.

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[*] Berichte der Deutschen Chem. Gesellschaft, i. 161.

Analytical Methods. — These are for the most part similar to those which I have already described. The three oxides may be precipitated together by mercurous nitrate and mercuric oxide, and then ignited with sodic tungstate in the manner described for the analysis of phospho-molybdates and arsenio-molybdates. The phosphoric oxide cannot be determined with accuracy by direct precipitation with magnesia-mixture. It is necessary first to remove the vanadic oxide. This may be done by dissolving the salt, adding ammonia in small but distinct excess, and afterward ammonic nitrate in large quantity. The solution is to be boiled for a short time, care being taken that after boiling free ammonia shall still be present. After standing in the cold for twenty-four hours the precipitated ammonic meta-vanadate may be filtered off, washed with a cold concentrated solution of ammonic nitrate, and titrated in the manner which I have described in speaking of the vanadio-molybdates. In the filtrate from the meta-vanadate phosphoric oxide may be determined by double precipitation with magnesia-mixture and final treatment with ammonic sulphide. Molybdic oxide is best determined by difference, the sum of the weights of the three oxides being known. Water, ammonia, and basic oxides may be found by the methods which I have already described in the cases of the binary compounds.

48 : 2 : 1 *Series.* — When 10 : 2 acid phospho-molybdate of ammonium, $10\,MoO_3 . 2\,P_2O_5 . 5\,(NH_4)_2O + 6$ aq., and ammonic meta-vanadate are dissolved together, there appears to be no reaction; but if a small excess of chlorhydric acid is added, and the solution is boiled, a beautiful deep orange-red crystalline precipitate is formed at once. This may be drained on a filter and washed with cold water, in which it is but slightly soluble. Hot water dissolves it rather more freely, but the salt cannot be purified by recrystallization, as it is more or less completely decomposed by solution. Ammonia water dissolves it, forming a colorless liquid, in which baric acetate produces a nearly colorless precipitate. Of this salt, —

1.3011 gr. lost on ignition with WO_4Na_2 0.1399 gr. = 10.75% $NH_3 + H_2O$

1.0425 gr. lost on ignition with WO_4Na_2 0.1124 gr. = 10.78% $NH_3 + H_2O$

1.5611 gr. gave 0.1361 gr. NH_4Cl = 4.24% $(NH_4)_2O$
1.0113 gr. “ 0.0900 gr. “ = 4.32% “
1.3997 gr. “ with MnO_4K 0.0304 gr. V_2O_5 = 2.17%
1.9173 gr. “ “ “ 0.0463 gr. “ = 2.41%
1.9173 gr. “ 0.1112 gr. $P_2O_7Mg_2$ = 3.71% P_2O_5

In the last two analyses the vanadic pentoxide was first separated by ammonic nitrate as VO_3NH_4; the phosphoric oxide was then determined in the filtrate.

The analyses correspond fairly well with the formula

$$48\ MoO_3 \, . \, 2\ P_2O_5 \, . \, V_2O_5 \, . \, 7\ (NH_4)_2O + 30\ aq.$$

		Calc'd.	Mean.	Found.	
48 MoO_3	6912	83.45	83.23	83.23 (diff.)	
2 P_2O_5	284	3.43	3.71	3.71	
V_2O_5	183	2.21	2.29	2.17	2.41
7 $(NH_4)_2O$	364	4.39	4.28	4.32	4.24
30 H_2O	540	6.52	6.50	6.50	6.51
	8283	100.00			

The compound may be regarded as a double salt, with the formula

$$2\{16\ MoO_3 \, . \, P_2O_5 \, . \, 2\ (NH_4)_2O \, . \, H_2O\} + 16\ MoO_3 \, . \, V_2O_5 \, . \, 3\ (NH_4)_2O + 28\ aq,$$

though, of course, other arrangements of the constituents are, in the present state of our knowledge, equally probable. Thus, we may also represent the results of the analyses by the expression,

$$2\{12\ MoO_3 \, . \, P_2O_5 \, . \, 2\ (NH_4)_2 \, . \, H_2O\} + 24\ MoO_3 \, . \, V_2O_5 \, . \, 3\ (NH_4)_2O + 28\ aq.$$

14 : 1 : 8 *Series.* — The beautiful yellow crystalline phospho-molybdates of ammonium, containing respectively twenty-four and twenty-two molecules of MoO_3 to one molecule of phosphoric oxide, slowly dissolve when boiled with a solution of ammonic meta-vanadate, giving a very fine deep orange-red liquid. After standing a few hours, the solution gives splendid deep ruby-red crystals in large quantity. These crystals appear to be octahedra; they dissolve readily in hot water to a deep orange-red liquid, without undergoing any apparent decomposition, and the salt crystallizes from the solution unchanged. The solution gives no precipitate at first with baric chloride, but after a time very fine garnet-red crystals are formed in small quantity, mixed

with a pale orange flocky or indistinctly crystalline substance, with an orange-red supernatant liquid. Potassic bromide in large excess gives an orange crystalline, and argentic nitrate a cinnamon-colored not distinctly crystalline precipitate. Mercurous nitrate and plumbic acetate give orange precipitates. A solution of chloride of trimethylammonium, $N(CH_3)_3HCl$, gives an orange precipitate in the concentrated solution, soluble in boiling water, and crystallizing in beautiful small granular crystals, which are orange with an aurora-red tint. The crystals of the ruby-red salt became duller upon the surfaces when dried on woollen paper, but did not distinctly effloresce. Of this salt, —

1.0686 gr. lost on ignition with WO_4Na_2 0.2833 gr. = 26.51% NH_3 and H_2O
1.3051 gr. gave 0.2245 gr. NH_4Cl = 8.36% $(NH_4)_2O$
1.1020 gr. " 0.3253 gr. V_2O_5 = 29.51%
1.1113 gr. " 0.0598 gr. $P_2O_7Mg_2$ = 3.44% P_2O_5

The analyses lead to the formula,

$$14\ MoO_3 \cdot P_2O_5 \cdot 8\ V_2O_5 \cdot 8\ (NH_4)_2O + 50\ aq.$$

		Calc'd.		Found.	
14 MoO_3	2016	40.83		40.54	
8 V_2O_5	1464	29.64	73.36	29.51	73.49
P_2O_5	142	2.89		3.44	
8 $(NH_4)_2O$	416	8.42		8.36	
50 H_2O	900	18.22		18.14	
	4938	100.00			

If we assume that in this salt vanadic pentoxide stands in a relation to phosphoric oxide exactly analogous to that of molybdic teroxide, the compound will be of the same type as the phospho-molybdate already described,

$$22\ MoO_3 \cdot P_2O_5 \cdot x\ R_2O,$$

since we may write V_2O_5 as if its rational formula were $V_2O_2 \cdot O_3$.

In some preparations of this salt I observed the formation of two other salts in relatively small quantity. One of these formed pale orange-colored needles; the other, glimmering scales but slightly soluble in hot water.

PHOSPHO-VANADIO-TUNGSTATES.

These compounds bear a general resemblance to the phospho-vanadio-molybdates already described, and may be prepared by similar processes. They have usually a more or less deep orange or orange-red color, and very often exhibit a peculiar and highly characteristic aurora-red tint. They are crystalline and well defined, and many salts of the different series are very beautiful.

Analytical Methods. — In all these salts it will, as in similar cases, be found most advantageous to determine the three acid-forming oxides by means of mercurous nitrate and mercuric oxide in the manner already pointed out. The estimation of phosphoric oxide may usually be made with a fair approximation to precision by direct precipitation with magnesia-mixture in the ammoniacal solution, redissolving the ammonio-magnesic phosphate, and precipitating a second time. In some cases I have found it better first to reduce the vanadic pentoxide to vanadic dioxide by boiling with strong chlorhydric acid, evaporating to dryness, and redissolving with the addition of a little tartaric and chlorhydric acids. A perfectly satisfactory method of estimating phosphoric oxide in these compounds remains to be discovered. Vanadic pentoxide may be estimated with accuracy by the methods already pointed out for the analysis of the vanadio-tungstates; that is, by boiling with strong chlorhydric acid, collecting the chlorine evolved in a solution of potassic iodide, and determining the free iodine by titrition with sodic hyposulphite. A solution of potassic hypermanganate does not always oxidize vanadic dioxide in presence of tungstic, phosphoric, and free sulphuric acid, or only with great difficulty, so that the method is not generally applicable for the analysis of this class of compounds. Nitric acid, however, readily oxidizes the dioxide under the same circumstances.

60 : 3 : 1 *Series.* — When the white insoluble phospho-tungstates of ammonium containing twenty-two or twenty-four molecules of tungstic to one of phosphoric oxide are dissolved in ammonia water, and a solution of ammonic meta-vanadate is added, no precipitate is formed; but if a small excess of chlorhydric acid is present in the boiling liquid, a fine lemon-yellow crystalline precipitate soon forms, which is to be well washed with a cold dilute solution of ammonic nitrate, as otherwise the salt passes readily through the filter, giving a milky liquid. The final washing may be made with a very dilute solution of the nitrate. After drying on woollen paper, the salt closely resembles tungstic oxide in color. It is almost insoluble in cold, and but slightly soluble in hot

water, but with a large excess of ammonic phosphate it dissolves to a yellow solution; with ammonia water it gives a colorless solution. In a solution of ammonic carbonate it dissolves with strong effervescence, indicating its distinctly acid character. The salt is not readily reduced by boiling with sulphuric and sulphurous acids, or by citric acid in the presence of chlorhydric acid, but easily by boiling with a strong solution of potassic cyanide, and, as is usual with this class of compounds, by fusion with the same salt.

Of this compound, —

2.0684 gr. lost on ignition with WO_4Na_2 0.2068 gr. = 10.00% NH_3 and H_2O
1.0971 gr. gave 0.0747 gr. NH_4Cl = 3.31% $(NH_4)_2O$
1.3424 gr. " 0.0568 gr. P_2O_7Mg = 2.71% P_2O_5
2.5488 gr. " 0.1102 gr. " = 2.77% "
1.0555 gr. " 0.0123 gr. V_2O_5 = 1.16%

The analyses correspond very closely to the formula,

$$60\ WO_3 \,.\, 3\ P_2O_5 \,.\, V_2O_5 \,.\, 10\ (NH_4)_2O + 60\ aq,$$

which requires: —

		Calc'd.		Found.		
60 WO_3	13920	86.29	90.00	86.10 (diff.)		90.00
3 P_2O_5	426	2.64		2.71	2.77	
V_2O_5	183	1.15		1.16		
10 $(NH_4)_2O$	520	3.23	9.92	3.31	10.00	
60 H_2O	1080	6.69		6.69		
	16129	100.00				

The compound is very probably a double salt, and may have the formula,

$$3\ \{16\ WO_3 \,.\, P_2O_5 \,.\, 3\ (NH_4)_2O\} + 12\ WO_3 \,.\, V_2O_5 \,.\, (NH_4)_2O \,.\, 2\ H_2O + 58\ aq.$$

The arrangement of the constituents is here, of course, purely arbitrary, and must be regarded as only provisional. In the analyses above given the phosphoric oxide was determined directly and by double precipitation. The vanadic oxide was determined by boiling with chlorhydric acid and titrition, in the manner already described.

16 : 1 : 3 *Series.* — A boiling solution of ammonic meta-vanadate dissolves the white insoluble phospho-tungstates of ammonium quite readily to a very deep orange-red solution. After standing some

days, large deep orange or garnet-red crystals separate in quantity. They appear to be octahedra, and when first separated from the mother liquor are very beautiful; but on standing in the air they lose their lustre, perhaps from a superficial effervescence, and become dull red. The salt is readily soluble in water, giving a deep orange-red solution, and crystallizes from the solution unchanged. The constitution of this salt is represented by the formula,

$$16\ WO_3 . 3\ V_2O_5 . P_2O_5 . 5\ (NH_4)_2O + 37\ aq,$$

as the following analyses show: —

1.0379 gr. lost on ignition with WO_4Na_2 0.1826 gr. = 17.59% NH_3 and H_2O
1.2811 gr. gave 0.1264 gr. NH_4Cl = 4.80% $(NH_4)_2O$
1.0652 gr. " 0.1074 gr. V_2O_5 = 10.08%
1.0130 gr. " 0.0419 gr. $P_2O_7Mg_2$ = 2.64% P_2O_5

The formula given requires: —

		Calc'd.		Found.	
16 WO_3	3712	69.67	82.62	69.69	82.41
3 V_2O_5	548	10.28		10.08	
P_2O_5	142	2.67		2.64	
5 $(NH_4)_2O$	260	4.88		4.80	
37 H_2O	666	12.50		12.79	
	5328	100.00		100.00	

Adopting the provisional hypothesis which I have proposed above, that V_2O_5 as $V_2O_2 . O_3$ may partially replace MoO_3 or WO_3 in these combinations, and that, on the other hand, V_2O_5 also replaces P_2O_5, we may write the formula given above,

$$8\ WO_3 . 2\ V_2O_2 . O_3 . P_2O_5 . 3\ (NH_4)_2O + \\ 8\ WO_3 . V_2O_5 . 2\ (NH_4)_2O . H_2O + 36\ aq,$$

in which formula the first term is reduced to the type of

$$10\ WO_3 . P_2O_5 . 3\ (NH_4)_2O.$$

The presence of five molecules of ammonic oxide shows that the salt belongs to the acid type so often met with in this class of compounds, and upon the view which I consider probable,* that the formulas of all the phospho-tungstates and phospho-molybdates as now received should be doubled, we should write the above formula

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* Proceedings, Vol. XVII. p. 89.

$$16\ WO_3\ .\ 2\ V_2O_2.O_3.V_2O_5.P_2O_5\ .\ 5\ (NH_4)_2O\ .\ H_2O + 36\ aq;$$

corresponding to

$$16\ WO_3\ .\ 2\ P_2O_5\ .\ 5\ (NH_4)_2O\ .\ H_2O.$$

I consider this view of the subject as most probable in the present state of our knowledge.

60 : 3 : 2 *Series.* — When the 20 : 1 : 6 baric phospho-tungstate already described is boiled with vanadic hydrate, $VO(OH)_3$, the acid dissolves readily, and a beautiful orange-red solution is formed. On cooling, a salt separates in octahedral crystals, which have a very fine aurora-red color. The crystals dissolve rather easily in hot water, but are at the same time decomposed. A brownish orange salt then separates in distinct crystals, together with a white powder. The two can be separated mechanically. The mother liquor of the aurora-red salt yields on evaporation large dark-red crystals. Of the aurora-red salt,—

0.4165 gr. lost on ignition with WO_4Na_2 0.0540 gr. = 12.96%
1.1550 gr. " " " " 0.1500 gr. = 12.98%
0.8819 gr. gave of mixed oxides 0.6474 gr. = 73.41%
1.4699 gr. " " " 1.0784 gr. = 73.37%
1.5188 gr. " " " 1.1145 gr. = 73.38%
1.5188 gr. " of $P_2O_7Mg_2$ 0.0508 gr. = 2.14% P_2O_5
1.0522 gr. " of mixed oxides 0.7709 gr. = 73.26%
1.0522 gr. " of $P_2O_7Mg_2$ 0.0380 gr. = 2.31% P_2O_5
1.3324 gr. " of V_2O_5 by titrition 0.0258 gr. = 1.93%
0.2693 gr. " " " 0.0051 gr. = 1.87%

The analyses correspond to the formula

$$60\ WO_3\ .\ 3\ P_2O_5\ .\ 2\ V_2O_5\ .\ 18\ BaO + 144\ aq,$$

which requires : —

		Calc'd.		Mean.					
60 WO_3	13920	69 39	73.35	69.23	73.35	69.29	69.25	69.26	69.14
3 P_2O_5	426	2.14		2.22		2.14	2.31		
2 V_2O_5	366	1.82		1.90		1.93	1.87		
18 BaO	2754	13.73		13.68			13.68		
144 H_2O	2592	12.92		12.97		12.96	12.98		
	20058	100.00		100.00					

The baric oxide was determined by difference. In all determinations of the three acid oxides it was found necessary to ignite finally with a weighed quantity of normal sodic tungstate, in order to expel the mercuric oxide completely, and obtain a constant weight. The aurora-red salt may be regarded as a double compound, with the possible formula

$$3\ \{12\ WO_3 \,.\, P_2O_5 \,.\, 4\ BaO \,.\, 2\ H_2O\} + 2\ \{12\ WO_3 \,.\, V_2O_5 \,.\, 3\ BaO \,.\, 3\ H_2O\} + 132\ aq.$$

It has, I believe, the highest molecular weight, 20058, yet observed, though I shall describe a little farther on a phospho-vanadio-vanadico-tungstate with the formula

$$60\ WO_3 \,.\, 3\ P_2O_5 \,.\, V_2O_5 \,.\, VO_2 \,.\, 18\ BaO + 150\ aq,$$

with the molecular weight 20066. It will be interesting to determine the specific heats of bodies of this class, as well as the heat of formation. The formation of the aurora-red salt is very simply expressed by the equation,

$$3\ \{20\ WO_3 \,.\, P_2O_5 \,.\, 6\ BaO\} + 2\ V_2O_5 = 60\ WO_3 \,.\, 3\ P_2O_5 \,.\, 2\ V_2O_5 \,.\, 18\ BaO,$$

the process being one of simple addition.

I have mentioned above the fact that a dark red salt crystallizes from the mother liquor of the aurora-red salt. The following analytical results were obtained with the small quantity of this salt at my disposal: —

0.7660 gr. gave 0.5570 gr. mixed oxides = 72.71%
1.0405 gr. " 0.2133 gr. SO_4Ba = 13.45% BaO
1.0405 gr. lost on ignition 0.1451 gr. = 13.94%

In the orange-brown salt formed by the decomposition of the aurora-red salt,

1.1919 gr. lost on ignition with WO_4Na_2 0.1611 gr. = 13.51%
1.0476 gr. gave 0.7653 gr. mixed oxides = 73.05%
1.4122 gr. " 0.3078 gr. SO_4Ba = 14.31%
1.2372 gr. " 0.0087 gr. V_2O_5 = 0.70%

No formulas can be deduced from these analyses, but they may serve to identify the salts analyzed in future investigations.

18 : 3 : 4 *Series.* — The 24 : 1 phospho-tungstate of sodium already described, $24\ WO_3 \,.\, P_2O_5 \,.\, 2\ Na_2O \,.\, 4\ H_2O + 23\ aq$, is readily dissolved by boiling with a solution of ammonic meta-vanadate, and gives a deep orange-red liquid. This solution does not yield crys-

tals on evaporation, or after standing for some time. When, however, a solution of potassic bromide is added in large excess, a deep orange-red crystalline precipitate is quickly formed in large quantity. The salt exhibits the peculiar aurora-red tint which is often observed when phosphoric acid or a soluble phosphate is mixed with a solution containing both tungstic and vanadic oxides. The compound dissolves in a rather large proportion of hot water, but at the same time undergoes decomposition, and the solution after a time deposits a bright orange-brown crystalline salt without the peculiar aurora-red tint. The first-mentioned potassic salt, as precipitated from a cold solution, allowed to stand twenty-four hours, then washed with cold water and dried on woollen paper, gave on analysis the formula

$$18\ WO_3 \,.\, 4\ V_2O_5 \,.\, 3\ P_2O_5 \,.\, 8\ K_2O + 32\ aq,$$

which may perhaps be written

$$2\ \{6\ WO_3 \,.\, 2\ V_2O_5 \,.\, P_2O_5 \,.\, 3\ K_2O\} + 6\ WO_3 \,.\, P_2O_5 \,.\, 2\ K_2O \,.\, H_2O,$$

the type of the first compound being

$$8\ WO_3 \,.\, P_2O_5 \,.\, 3\ K_2O.$$

1.1017 gr. lost on ignition with WO_4Na_2 0.0973 gr. = 8.83%
1.0803 gr. gave 0.8646 gr. mixed oxides = 80.03%
1.1159 gr. " 0.1218 gr. V_2O_5 = 10.91%
1.2104 gr. " 0.1227 gr. $P_2O_7Mg_2$ = 6.48%

The formula given requires: —

		Calc'd.		Found.	
18 WO_3	4176	62.68		62.64	
4 V_2O_5	732	10.99	80.06	10.91	80.03
3 P_2O_5	426	6.39		6.48	
8 K_2O	752	11.29		11.14	
32 H_2O	576	8.65		8.83	
	6662	100.00			

7 : 1 : 1 *Series.* — The bright orange-brown salt formed by the decomposition of the 18 : 4 : 3 salt was in small distinct granular crystals. Of this salt, —

0.9773 gr. lost on ignition with WO_4Na_2 0.0780 gr. = 7.98%
1.0160 gr. gave 0.8205 gr. mixed oxides = 80.76%
1.3077 gr. " 0.1037 gr. V_2O_5 = 7.93%
1.0113 gr. " 0.0958 gr. $P_2O_7Mg_2$ = 6.06% P_2O_5

The analyses correspond, though not very closely, to the formula

$$7\ WO_3 \,.\, V_2O_5 \,.\, P_2O_5 \,.\, 3\ K_2O + 11\ aq,$$

which requires : —

		Calc'd.		Found.	
7 WO_3	1624	66.86	80.23	66.77	80.76
V_2O_5	183	7.53		7.93	
P_2O_5	142	5.84		6.06	
3 K_2O	282	11.61		11.26	
11 H_2O	198	8.16		7.98	
	2429	100.00			

According to the view which I have taken as to the function of V_2O_5 in this class of compounds, the 7 : 1 : 1 potassic salt belongs to the type

$$8\ WO_3 \,.\, P_2O_5 \,.\, 3\ K_2O,$$

$V_2O_2 \,.\, O_3$ taking the place of one molecule of WO_3. A much more extended study will be necessary to test this hypothesis. The vanadio-phospho-tungstates are probably numerous, and from their great beauty, as well as from their theoretic interest, form an attractive subject for investigation. The following notes may serve to furnish fresh points of departure. When the solution of vanadio-tungstate of sodium (obtained by boiling 12 : 5 acid sodic tungstate with the mixed oxides of vanadium and oxidizing completely with bromine) is mixed with a solution of hydro-disodic phosphate, no apparent action takes place; but on boiling, the orange solution takes a deep red color, and soon deposits splendid ruby-red crystals in quantity. These crystals are decomposed in part even by cold water, which appears to separate phosphoric acid or sodic phosphate. An orange-colored sodium salt then separates. Almost exactly the same results are obtained when a solution of vanadio-tungstate of ammonium is boiled with a solution of ammonic phosphate. The liquid takes a beautiful deep red tint, and soon deposits splendid ruby-red crystals. The solution of the sodium salt, after a day or two, gives with one of trimethyl-ammonium chloride, $N(CH_3)_3HCl$, very fine granular ruby-red crystals. Of these crystals,

0.9752 gr. gave 0.8549 gr. mixed oxides = 87.66%
1.1543 gr. " 0.0631 gr. V_2O_5 = 5.46%
1.0061 gr. " 0.0552 gr. $P_2O_7Mg_2$ = 3.51%

The loss corresponding to water and trimethyl-ammonium oxide is 12.34%. The ratio of the three oxides, WO_3, V_2O_5, and P_2O_5, is

$34\ WO_3 \,.\, 3\ V_2O_5 \,.\, 2\ P_2O_5$; but a determination of the trimethylammonium oxide will be necessary in order to settle the formula completely. I am indebted to the kindness of Prof. Arthur Michael for a supply of the trimethylamin salt, which has proved of great service to me. The disposition of the corresponding oxide to form well-crystallized salts makes it a valuable test, and it should become an article of commerce for chemists' use.

VANADIO-VANADICO-MOLYBDATES.

The salt about to be described constitutes the type of a new and extensive series of complex acids, which contain two different linking oxides, embraced respectively under the formulas R_2O_5 and $R'O_2$, in which, however, R and R′ may be identical. The general formula for this class of molybdenum compounds may be written

$$m\ MoO_3 \,.\, n\ R_2O_5 \,.\, p\ R'O_2 \,.\, x\ R''_2O,$$

which, in the case of the identity of R and R′, becomes

$$m\ MoO_3 \,.\, n\ R_2O_5 \,.\, p\ RO_2 \,.\, x\ R''_2O.$$

I shall show that these are corresponding salts, containing tungsten in place of molybdenum. Vanadio-vanadico-molybdates are very readily formed by boiling a mixture of the two oxides of vanadium with an acid molybdate; by the partial reduction of vanadio-molybdates; or by digesting solutions of acid molybdates with solutions which contain vanadic dioxide and pentoxide.

28 : 4 : 1 *Vanadio-vanadico-molybdate of Ammonium.*—When pure ammonic divanadate is ignited in an open platinum vessel, and the remaining mass is boiled with an excess of a solution of 14 : 6 acid ammonic molybdate, a greenish solution is formed, which after filtration and evaporation yields on cooling a pale greenish-yellow crystalline salt. After draining on the filter-pump, the salt may be redissolved and recrystallized, when it presents very distinct granular greenish-yellow crystals. The solution is bright yellow. Of this salt,—

1.4613 gr. lost on ignition with WO_4Na_2 0.2527 gr. = 17.29%
1.3326 gr. gave by titrition 0.1423 gr. $(NH_4)_2O$ = 10.68%
1.2031 gr. " " 0.1288 gr. " = 10.71%
2.1968 gr. " 0.2184 gr. V_2O_5 = 9.95% $VO_2 + V_2O_5$
0.9980 gr. " 0.0607 gr. VO_2 = 6.08% VO_2

The analyses lead to the formula

$$28\ MoO_3 \cdot 4\ V_2O_5 \cdot VO_2 \cdot 11\ (NH_4)_2O + 20\ aq,$$

which requires: —

		Calc'd.	Found.	
28 MoO_3	4032	73.56	73.34	
4 VO_2	334	6.09	6.08	
V_2O_5	183	3.34	3.29	
11 $(NH_4)_2O$	572	10.44	10.68	10.71
20 H_2O	360	6.57	6.60	
	5481	100.00		

The compound is doubtless to be regarded as a double salt, but there are at present no data upon which to base even a conjectural arrangement. The salt is slightly soluble in cold water, the solution being strongly acid to litmus paper. It is soluble in hot water, and separates from the solution without sensible decomposition. The solution is reduced with great difficulty, either by sulphurous oxide or by sulphydric acid gas. For analysis I found it best, after oxidation with nitric acid, to boil with excess of ammonia, evaporate with ammonic chloride, and separate the ammonic meta-vanadate upon an asbestos filter. The vanadium was then determined by titrition with hypermanganate. The vanadic dioxide was determined by hypermanganate in the solution of the salt, after adding phosphoric and sulphuric acids. It was found necessary to use very dilute solutions, and the close agreement of the determination of vanadic dioxide with the formula cannot be regarded as other than accidental. The reactions of this salt are as follows: the cold dilute solution gives no precipitate with salts of zinc, copper, manganese, and cadmium; a pale yellow flocky precipitate with baric chloride, which soon becomes granular-crystalline; with potassic bromide, after some days, very fine, large prismatic crystals; with argentic nitrate, the solution gives a flocky precipitate, which is yellow with a tinge of buff; with mercurous nitrate, a bright, and with thallous nitrate, a pale yellow, flocky precipitate.

15 : 1 : 2 *Vanadio-vanadico-molybdate of Barium.* — Baric chloride added to the mother liquor from which the preceding salt was prepared gave a pale yellow crystalline, and, so far as could be seen, homogeneous precipitate, in very small grains. This was filtered off, well washed with cold water, and dried on woollen paper for analysis. The filtrate was greenish, and gave no other salt on evapo-

ration. The barium salt is very slightly soluble in cold water, and is decomposed by boiling water, with separation of baric molybdate, and formation of a pale greenish-yellow solution, which possibly contains a new salt of the same class. The salt is decomposed by boiling with mercurous nitrate, giving a bright yellow crystalline body. Boiled with argentic nitrate it gives an orange-colored precipitate, which is also crystalline. Of this salt, —

1.1690 gr. gave 0.7260 gr. $WO_3 + V_2O_5 + VO_2$ = 62.09%
and 0.4772 gr. SO_4Ba = 26.80% BaO
1.5526 gr. gave 0.6332 gr. " = 26.70% "
1.0341 gr. lost on ignition 0.1127 gr. = 10.90% H_2O
2.1990 gr. gave by titrition 0.1748 gr. = 7.95% V_2O_5

The titrition was effected by $SO_4H_2 + SO_4(NH_4)_2 + 6$ aq, in a solution to which HCl had been added, after oxidation with nitric acid and addition of an excess of sodic carbonate. All the vanadium present was therefore estimated as V_2O_5.

The analyses correspond closely to the formula

$$30\ MoO_3 \,.\, 2\ V_2O_5 \,.\, 3\ VO_2 \,.\, 14\ BaO + 48\ aq,$$

which requires: —

		Calc'd.	Found.	
30 MoO_3	4320	54.40	54.40	(diff.)
2 V_2O_5	366	4.62	4.73	
3 VO_2	249	3.13	3.22	
14 BaO	2142	26.97	26.70	26.80
48 H_2O	864	10.88		10.90
	7941	100.00		

The compound is doubtless a double salt, and its formula may perhaps be

$$2\ \{6\ MoO_3 \,.\, V_2O_5 \,.\, 4\ BaO \,.\, 2\ H_2O\} + 3\ \{6\ MoO_3 \,.\, VO_2 \,.\, 2\ BaO \,.\, 4\ H_2O\} + 32\ aq;$$

only it must be remarked that the empirical formula given above must be doubled in order to obtain a symmetrical structural formula, as the number of molecules of vanadic dioxide is uneven in the simpler expression given.

VANADIO-VANADICO-TUNGSTATES.

The class of salts to which I have given this name come also under the general formula

$$m\ RO_3 . n\ R'_2O_5 . p\ R''O_2 . x\ R'''_2O,$$

and constitute, like the corresponding compounds containing molybdenum, a new ternary series. They are formed under the same conditions as these last, and like these have an orange or orange-red color, with a more or less distinct tinge of green.

12 : 2 : 3 (?) *Vanadio-vanadico-tungstate of Sodium.* — This salt, which was the first which I obtained containing vanadium, was formed by boiling with 12 : 5 acid sodic tungstate, a commercial vanadic pentoxide, which I owed to the kindness of Dr. J. Lawrence Smith, and which was probably prepared by igniting ammonic meta-vanadate, and therefore contained a certain proportion of vanadic dioxide. I did not succeed in preparing it a second time with a new preparation of the mixed oxides, and therefore trust that the incomplete analyses and meagre description of this and the corresponding ammonium and silver salts will be excused. The solution of the mixed oxides in the acid tungstate gave a deep orange-red solution, which, on evaporation to the consistency of a syrup, yielded after a time large orange-red apparently triclinic crystals, extremely soluble in water, and crystallizing only from syrupy solutions. In this salt, twice recrystallized, —

0.5968 gr. lost on ignition to fusion of the residue 0.1019 gr. = 17.07%
0.6852 gr. " " " " 0.1164 gr. = 16.99%
0.3311 gr. gave 0.2481 gr. $WO_3 + V_2O_5 + VO_2$ = 74.96%

These analyses, taken in connection with those of the ammonium and silver salts, may, with at least a certain degree of probability, be considered as leading to the formula

$$12\ WO_3 . 2\ V_2O_5 . 3\ VO_2 . 6\ Na_2O + 43\ aq,$$

which requires: —

		Calc'd.	Found.	
12 WO_3	2784	74.79	74.96	
2 V_2O_5	366			
3 VO_2	249			
6 Na_2O	372	8.18	8.05	
43 H_2O	774	17.03	16.99	17.07
	4545	100.00		

The solution of this salt had a deep orange-red color with distinct greenish reflections. Bromine water instantly gave a very fine deep orange solution, having nearly the color of potassic dichromate, and without the greenish tint: the liquid then contained only a sodic vanadio-tungstate. The solution gave flocky precipitates with various salts of heavy metallic oxides, and a bright red crystalline precipitate with argentic nitrate. A solution of acid potassic tungstate dissolved the mixture of oxides of vanadium, forming a greenish-orange solution, which also became bright orange-red with bromine. The potassic salt crystallized from this solution after evaporation to the consistency of a syrup, and gave crystals of a peculiar greenish-orange tint. The solution of this salt gave a bright orange indistinctly crystalline precipitate with mercurous nitrate. This precipitate was decomposed by dilute chlorhydric acid, yielding a yellow solution from which no crystals were obtained by evaporation. This is perhaps the acid of the series.

12 : 2 : 3 (?) *Ammonium Salt.* — 12 : 5 acid ammonic tungstate was boiled with a portion of the same commercial vanadic oxides in excess. The oxides dissolved readily, leaving, as in the cases of the sodium and potassium salts, a quantity of a black insoluble powder. The deep orange-yellow solution deposited on cooling beautiful orange-colored crystals of an ammonium salt; but on evaporating the main solution *in vacuo*, two kinds of crystals were obtained, one in relatively large dark-red octahedrons, the other much lighter-colored and resembling potassic dichromate. The darker salt gave in two analyses 17.98 and 18.05% of water and ammonic oxide. Of the lighter-colored salt separated mechanically from the first-named, —

0.8429 gr. lost on ignition 0.1149 gr. = 13.63% H_2O and NH_3
0.8164 gr. " " 0.1107 gr. = 13.56% " "
0.9047 gr. gave 0.1502 gr. NH_4Cl = 8.07% $(NH_4)_2O$

The analyses agree, so far as they go, very well with the formula,

$$12\ WO_3 \,.\, 2\ V_2O_5 \,.\, 3\ VO_2 \,.\, 6\ (NH_4)_2O + 12\ aq,$$

which requires: —

		Calc'd.	Found.
12 WO_3	2784	86.55	86.41 (diff.)
2 V_2O_5	366		
3 VO_2	249		
6 $(NH_4)_2O$	312	7.94	8.07
12 H_2O	216	5.51	5.52
	3927	100.00	

The solution of this salt gives a beautiful scarlet precipitate with argentic nitrate, and a fine yellow precipitate with salts of strychnin, which after standing some hours becomes granular crystalline.

12 : 2 : 3 (?) *Vanadio-vanadico-tungstate of Silver.* — The salt analyzed was in beautiful scarlet crystals, and was prepared by precipitating the ammonium salt with argentic nitrate, and washing with cold water. The salt is not distinctly crystalline when first thrown down, but becomes so after standing in the liquid. It is very slightly soluble in cold water, but dissolves in much hot water to a yellow liquid. Of this salt, —

2.1193 gr. lost on ignition 0.0621 gr. = 2.93%
0.7511 gr. gave 0.7420 gr. AgCl = 28.21% Ag_2O

These analyses agree with the formula,

$$12\ WO_3 \,.\, 2\ V_2O_5 \,.\, 3\ VO_2 \,.\, 6\ Ag_2\ O + 8\ aq,$$

which requires: —

		Calc'd.	Found.
12 WO_3	2784	68.87	68.86 (diff.)
2 V_2O_5	366		
3 VO_2	249		
6 Ag_2O	1392	28.21	28.21
8 H_2O	108	2.92	2.93
	4935	100.00	

The analyses which I have given may not be considered as sufficiently complete to establish the formulas assigned, but they serve to prove the existence of at least one class of vanadio-vanadico-tungstates. In substances of such high molecular weights the agreement between the formulas of three different salts prepared under precisely the same conditions has a certain value, but it is less conclusive than when the molecular weight is lower, because such a change as is produced by writing, for instance, 2 VO_2 for V_2O_5, does not greatly affect the percentage results. If we admit the correctness of the formulas given, it will still be necessary to double them in order to construct a structural formula which shall be symmetrical, since the number of molecules of VO_2, either free or contained in V_2O_5, is uneven. For the complete analysis of compounds of this class it will be most advantageous to determine the vanadic pentoxide by heating with strong chlorhydric acid in the manner already indicated, and then to determine the dioxide in another portion by means of hypermanganate, if possible, or by first oxidizing with bromine, and then determining the whole of the vanadium as pentoxide by boiling with chlorhydric acid and titrating as before.

PHOSPHO-VANADIO-VANADICO-TUNGSTATES.

I have given this rather ponderous appellation to a class of compounds in which vanadium exists partly as pentoxide and partly as dioxide. They may be regarded simply as double salts, but in the present state of our knowledge it will be found most convenient to consider them as a special class.

Salts of this type are formed whenever phospho-tungstates are mixed with vanadates in presence of vanadic dioxide, when vanadio-vanadico-tungstates are heated with solutions of alkaline phosphates or with phosphoric acid, and when phospho-vanadates and alkaline tungstates are brought together in presence of a reducing agent and of an acid. The salts are sometimes green and sometimes orange-red. In the last case they have frequently the peculiar aurora-red tint noticed among the colors of the phospho-vanadio-tungstates. They pass readily by oxidation with bromine or nitric acid into salts of the last-mentioned type, and they may be also derived from these by a partial reduction of the vanadic pentoxide.

Analytical Methods. — These are essentially the same as those which have been described. All the non-basic oxides may be determined together by means of mercurous nitrate and mercuric oxide, after complete oxidation with nitric acid. Phosphoric oxide may usually be determined directly, or after separation of a non-alkaline base, by double precipitation with magnesia-mixture. The vanadic pentoxide can be estimated by boiling with chlorhydric acid and titrition in the manner already pointed out. To determine the vanadic dioxide the solution must first be oxidized completely, so as to convert the dioxide into pentoxide, any excess of the oxidizing agent employed being carefully removed. I prefer to use bromine water for this purpose. The whole of the vanadium may then be determined by titrition as above. The difference between the amount of vanadic pentoxide found before and after complete oxidation then gives, by a simple proportion, the corresponding amount of vanadic dioxide. It must be remembered that the sum of the non-basic oxides found by the mercury process requires to be corrected by adding the amount of oxygen required to convert the vanadic dioxide present into the equivalent of pentoxide. When the whole quantity of vanadium present is small, this correction may be neglected, as falling within the limits of the errors of analysis unavoidable with our present methods. Baric oxide in these salts is best estimated by difference, as the direct estimation almost always gives too high a percentage.

60 : 3 : 1 : 1 *Barium Salt.* — When ammonic vanadate is heated in a porcelain crucible until all the ammonia is expelled, the greenish residue consists, as already stated, chiefly of a mixture of vanadic dioxide and pentoxide. If this mixture be added in small portions at a time to a boiling solution of the baric phospho-tungstate, $20\ WO_3 . P_2O_5 . 6\ BaO$, already described, the liquid takes at once a rather dull green color. The filtrate from the excess of mixed oxides, after evaporation in a water-bath and standing for some hours, yields a mass of deep green crystals, mechanically mixed with a relatively small proportion of a fine white powder, which may easily be removed by washing with cold water and pouring off the powder in suspension. The dark green crystals are regular octahedrons, frequently in long aggregates and beautifully defined. The salt is rather insoluble in cold but readily soluble in hot water, with a dark and rather dull green color. The cold solution, after adding dilute sulphuric acid, is not sensibly oxidized by potassic hypermanganate or in alkaline solution by iodine. The hot solution is oxidized by bromine and by nitric acid, and becomes deep orange-red. At a boiling heat potassic hypermanganate also oxidizes it, the quantity required for oxidation being very small, so that it can with difficulty be estimated. Of this salt, —

1.2596 gr. gave 0.9178 gr. mixed oxides = 72.86%
1.0160 gr. lost on ignition 0.1362 gr. = 13.40%
1.4649 gr. “ “ 0.1969 gr. = 13.44%
1.8580 gr. gave 0.0624 gr. $P_2O_7Mg_2$ = 2.15% P_2O_5
1.3846 gr. “ 0.0105 gr. V_2O_5 = 0.76%
1.1972 gr. “ 0.0131 gr. “ = 1.09%

In these analyses the vanadic pentoxide was determined directly in the salt, by boiling with chlorhydric acid and titrating. In two other analyses, the vanadic dioxide was first completely oxidized by means of bromine ; the whole quantity of vanadium was then determined as before. The percentage of vanadic dioxide was then calculated from the excess of V_2O_5 over that found by direct analysis. In this process, —

1.1379 gr. gave 0.0161 gr. V_2O_5 = 1.44%
1.1714 gr. “ 0.0200 gr. “ = 1.71%

The analyses correspond very closely to the formula,

$$60\ WO_3 \cdot 3\ P_2O_5 \cdot V_2O_5 \cdot VO_2 \cdot 18\ BaO + 150\ aq,$$

which requires: —

		Calc'd.	Found.	
$60\ WO_3$	13920	69.37	69.32	
$3\ P_2O_5$	426	2.12	2.15	
V_2O_5	183	0.92	1.09	0.76
VO_2	83	0.42	0.46	
$18\ BaO$	2754	13.72	13.72	
$150\ H_2O$	2700	13.45	13.40	13.44
	20066	100.00		

The baric oxide is estimated by difference. The relation of this salt to the aurora-red octahedral phospho-vanadio-tungstate of barium already described is interesting. We have respectively the formulas,

$$60\ WO_3 \cdot 3\ P_2O_5 \cdot V_2O_5 \cdot V\ O_2 \ \cdot 18\ BaO + 150\ aq,$$
$$60\ WO_3 \cdot 3\ P_2O_5 \cdot V_2O_5 \cdot V_2O_5 \cdot\ 18\ BaO + 144\ aq,$$

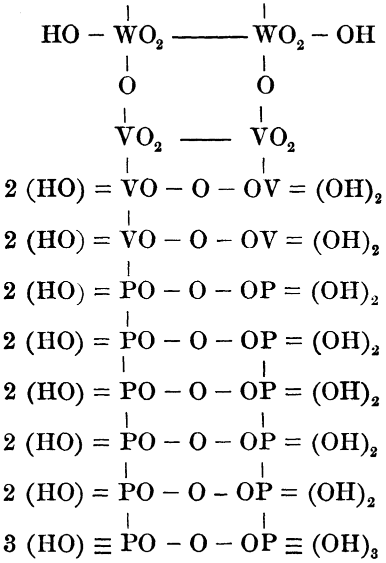
and it is easy to see how, at least theoretically, one salt could be prepared from the other. With respect to the rational constitution of the green salt, it is possible at present only to form a provisional hypothesis. I am disposed to regard it as a triple compound, and to assign to it the formula,

$$3\ \{12\ WO_3 \cdot P_2O_5 \cdot 3\ BaO \cdot 3\ H_2O\} + 12\ WO_3 \cdot V_2O_5 \cdot 5\ BaO \cdot H_2O + 12\ WO_3 \cdot VO_2 \cdot 4\ BaO$$

In this formula all the terms correspond to known compounds, the last to the dodeka-silico-tungstate type established by Marignac, VO_2 replacing SiO_2. Of course, as in similar cases, various other formulas may be proposed. I lay no particular stress upon the view I have taken, which a wider and deeper study of these compounds may prove to be untenable. The formation of the salt may be expressed by the equation,

$$3\ \{20\ WO_3 \cdot P_2O_5 \cdot 6\ BaO\} + V_2O_5 + VO_2 = 60\ WO_3 \cdot 3\ P_2O_5 \cdot V_2O_5 \cdot VO_2 \cdot 18\ BaO.$$

The formula must be doubled to permit of a representation by means of a symmetrical structural formula. If we omit all the molecules of tungstic oxide except two, in order to save space, the linking portion of the structural formula of the corresponding acid may be written as follows: —



$$\begin{array}{rcccl}
 & | & & | & \\
HO - & WO_2 & \text{———} & WO_2 & - OH \\
 & | & & | & \\
 & O & & O & \\
 & | & & | & \\
 & VO_2 & \text{——} & VO_2 & \\
 & | & & | & \\
2\,(HO) = & VO & - O - & OV & = (OH)_2 \\
 & | & & & \\
2\,(HO) = & VO & - O - & OV & = (OH)_2 \\
 & | & & & \\
2\,(HO) = & PO & - O - & OP & = (OH)_2 \\
 & | & & & \\
2\,(HO) = & PO & - O - & OP & = (OH)_2 \\
 & | & & | & \\
2\,(HO) = & PO & - O - & OP & = (OH)_2 \\
 & | & & | & \\
2\,(HO) = & PO & - O - & OP & = (OH)_2 \\
 & | & & | & \\
2\,(HO) = & PO & - O - & OP & = (OH)_2 \\
 & | & & | & \\
3\,(HO) \equiv & PO & - O - & OP & \equiv (OH)_3
\end{array}$$

This formula, which, like most of those which I have given, is purely conjectural, will at least serve to show how the two different states of oxidation of vanadium may be represented in the combination, and how the basicity of PO and VO may be affected by their position. Such formulas are not without value, as suggesting the possibility of forming new combinations, even if, as I prefer in this case to do, we consider the salt represented as double or triple. Structural formulas for double and still more for triple inorganic salts would probably be still more complex, and what I have aimed at is to show how all the valences may be satisfied in an arbitrarily selected compound containing four oxides of three different types.

The general results deducible from the formulas which I have given in the present instalment of my work are as follows:—

1. Hypophosphorous and phosphorous acids may enter into combination with tungstic and molybdic oxides as links, so as to form complex inorganic acids. The structure of these four classes of acids indicates the possibility of forming new series of acids, in which methyl and other organic radicals or residues may take the place of the constitutional hydrogen of the hypophosphorous and phosphorous

linking terms, and again of others in which, besides the replacement of hydrogen, phosphorus may be replaced by arsenic, and possibly by antimony and other elements.

2. Vanadium may replace phosphorus and arsenic so as to form well-defined series of vanadio-molybdates and vanadio-tungstates embraced under the general formula

$$m\ RO_3 \cdot n\ V_2O_5 \cdot p\ R^1{}_2O.$$

3. Vanadic and phosphoric pentoxides may enter simultaneously into combination with tungstic or molybdic oxide, so as to form classes of triple acids embraced under the general formula

$$m\ RO_3 \cdot n\ P_2O_5 \cdot p\ V_2O_5 \cdot v\ H_2O.$$

4. A class of quadruple acids exists into which, in addition to phosphoric and vanadic pentoxides, vanadic dioxide may enter, the general formula being

$$m\ RO_3 \cdot n\ P_2O_5 \cdot p\ V_2O_5 \cdot r\ VO_2 \cdot v\ H_2O.$$

5. In another class of ternary or triple acids molybdic or tungstic oxide may be combined with both vanadic pentoxide and vanadic dioxide, the general formula being

$$m\ RO_3 \cdot n\ V_2O_5 \cdot p\ VO_2 \cdot v\ H_2O.$$

I shall show hereafter that all of these results are capable of further generalization; that, for example, other oxides of the types RO_2 corresponding to hydrates of the form $R(OH)_4$ may replace VO_2 or $V(OH)_4$; that other pentoxides may replace P_2O_5, As_2O_5, and V_2O_5, either in the presence or in the absence of oxides of the type RO_2; in short, that the complex inorganic acids form a new department of inorganic chemistry, and not a series of isolated compounds.

(*To be continued.*)